

Efficacy of Activated Carbon from Broiler Litter in the Removal of Litter Generated Ammonia

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Abstract. Over the past 10 years, the production of broilers has increased by 29 percent to approximately 9 billion in 2005. Ammonia (NH₃) pollution from broiler excreta is a primary concern for industry viability which requires innovative treatment options. This research focused on the use of broiler litter as activated carbon (BAC) to reduce aerial NH₃ generated by litter, an opportunity to not only reuse the manure, but also treat the emissions from or within broiler houses. The use of activated carbon in the removal of NH₃, specifically in broiler houses, has long been discarded primarily due to the high cost and low efficiency of the carbons. However, the study of BAC is a relatively new field that has focused on the removal of organics and/or metals from water. The objective of this study was to evaluate the efficacy of BAC to remove NH₃ volatilized from litter samples in a laboratory acid-trap system. The BAC is a much cheaper alternative than commercially produced activated carbons. Preliminary studies using NH₃/air mixture indicated that the BAC capacity to adsorb NH₃ was approximately double that of Vapure 612, a commercial carbon. In the litter emission study, the BAC and Vapure performance was comparable. The NH₃ emission reductions using the activated carbon columns were 25% for BAC and 36% for Vapure relative to the litter only control. The results of the study demonstrate the potential for a cyclical waste utilization strategy in using broiler litter activated carbon to capture NH₃ volatilized from litter.

Keywords. Broiler litter, ammonia, activated carbon, adsorption, emission

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Introduction

The development of activated carbons from waste sources is not a new field, yet it is slowly emerging as one of interest to those looking for a more economical source material with effective treatment capabilities (Bilitewski, 1979; Chiang and You, 1987; Jeyaseelan and Qing, 1996; Tay et al., 2001a and 2001b; Chen et al., 2002; Martin et al., 1996 and 2003; Rozada et al., 2003; Lima and Marshall, 2005). The use of agricultural by-products such as pecan shells, rice hulls and sugar cane bagasse as alternative sources for carbon has been investigated. These carbons were assessed for the capabilities with regard to metals and organics uptake and were found to be comparable to or better than commercial grade carbons (Johns et al., 1998; Toles et al., 1999; Ahmedna et al., 2000).

Economic NH₃ control technologies are genuinely lacking for the broiler industry. Historically, NH₃ control was accomplished through dilution with fresh air, but this can be associated with higher heating costs in addition to negative environmental stimuli. Commercial chemical litter treatments gained popularity in the last decade for temporary control of NH₃, where the control is proportional to application rate for acidifying agents such as aluminum sulfate, sodium bisulfate, and sulfuric acidified clay (McWard and Taylor, 2000). More recently, wet scrubbers have been proposed or evaluated for removing NH₃ at broiler house exhaust fans (Benson et al., 2005; Moore et al., 2006).

Multiple issues, such as reliable measurement and viable comparisons among estimates in addition to cost-effective remediation, surround NH_3 generation from litter. Ammonia may negatively impact aquatic, terrestrial, and atmospheric domains by eutrophication, soil acidification, and aerosol formation. Unlike traditional litter utilization as an organic fertilizer, the proposed research employs a cyclical concept, using the litter product as a solution to litter generated NH_3 . The objectives of the work were (1) to determine the effectiveness of activated carbon made from broiler litter (BAC) in adsorbing NH_3 from a gas standard and compared to a commercially available carbon; and (2) to establish data for the efficacy of BAC to capture litter generated NH_3 .

Materials and Methods

Materials. The broiler litter for producing the BAC was obtained from a commercial farm in Mississippi, where the original bedding was pine shavings. The broiler litter as collected had a moisture content of 25 to 30%. The commercial carbon, Vapure 612 carbon (Norit Americas, Marshall, Texas), is a steam activated coal-based carbon manufactured for use in the removal of odors, toxic vapors, irritants, and corrosive gases. For the litter emission test, litter samples were collected from a commercial Mississippi farm where the bedding origin was also pine shavings. Eleven flocks had previously been grown on the litter. The pH and moisture content were 8.32 and 17.9%, respectively. The litter samples were placed in the acid trap system described below to determine the capture capacity of the carbons for NH_3 volatilized from the litter.

BAC Drying and Pelletization. Broiler litter was dried to a moisture content of less than 10% in order to be milled in a Retsch cross-beater mill (Glen Mills, Clifton, NJ) to a particle size of less than US 20 mesh (<1 mm). The manure was then rehydrated to obtain a moisture level of 15 to 25%, determined to be ideal for efficient pelletization of this type material. Moisture content was monitored by using a Sartorius Moisture Analyzer model MA 51 (Sartorius, Brentwood, NJ). The samples were pelletized in a PMCL5 Lab pellet mill (California Pellet Mill, Merrimack, NH) equipped with a 5 mm die plate. The pellets produced were cylindrical with an approximate diameter of 5 mm and length of 5 mm.

BAC Pyrolysis and Activation. Individual samples of the pelletized manure were placed in a ceramic evaporating dish and then placed in a bench furnace equipped with a retort (Lindberg/Blue M, Watertown, WI). Pellets were pyrolyzed at 700°C for one hour under a flow of nitrogen gas set at a flow rate of $0.1 \text{ m}^3/\text{hr}$. Steam activation was conducted by injecting water at a flow rate of $3 \text{ mL}/\text{min}$ using a peristaltic pump into a flow of nitrogen gas entering the heated retort. Pyrolyzed chars were activated at 800°C for 45 min. The optimum activation conditions were determined from previous studies using copper adsorption rates and BET surface area analysis (Lima and Marshall, 2005). Activated carbons were allowed to cool to room temperature overnight in the retort. The carbons were then acid washed in a 0.8 N HCl solution for one hour, then rinsed in three one hour intervals to remove ash from the carbon surfaces. The carbons were then dried in a convection oven at 100°C overnight. Prior to analysis, the carbon was milled and sieved to a particle size between 1000 and $420\mu\text{m}$ (18×40 U.S. mesh) to ensure a consistent product.

Direct Adsorption Tests. In the direct NH_3 adsorption phase of the experimentation, 10 grams of the activated carbon created as stated above was placed in a column (Scienceware polyethylene 4" drying tubes) and bracketed on either end with glass wool (Figure 1). It should be noted the carbon amounts were prepared on a weight basis and the variance in the column lengths is due to interstitial space differences. The flow was also an important factor and in all cases the flow through the carbon column was mirrored by the flow through the sand blanks.

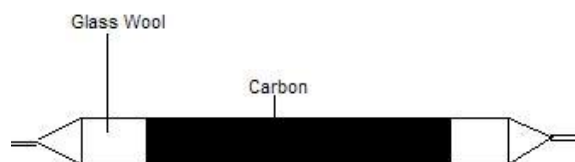


Figure 1. Schematic of the carbon adsorption column.

The column was then exposed to an NH_3 /air mixture at an average flow of $7204 \text{ mL}/\text{min}$. This flow rate resulted in an average of $6.96 \text{ mg N}/\text{minute}$. The flow from the column was passed through the boric acid (H_3BO_3) indicator solution. The system configuration may be found in Figure 2.

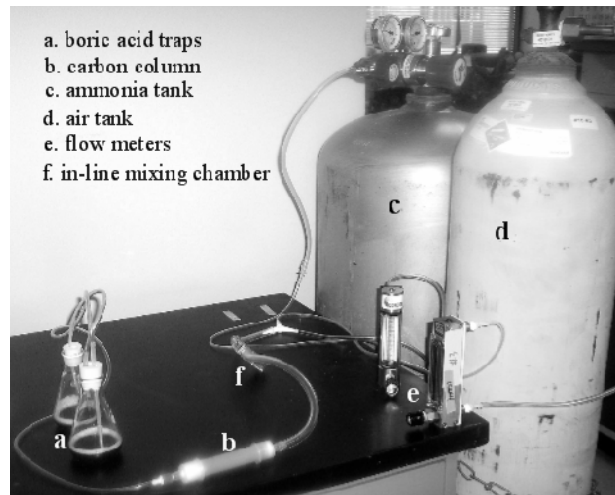


Figure 2: Direct ammonia adsorption components.

The boric acid solution was titrated with 0.1 N hydrochloric acid to determine the mg of N in the solution. The acid trap/titration components were adapted from the method, described below for determining litter emissions. Sand washed with deionized water and dried overnight in a vacuum oven at 85°C was sieved to 1000 and 420µm (18 x 40 U.S. mesh) and used as the blank. The commercial carbon Vapure 612, a non-specific carbon, was used for comparison. The use of sand in the column blanks ensures the flow rates are the same as those in the carbon columns. The NH₃ results from the sand blank titrations determine the initial or influent NH₃ concentrations. See Table 1 below for column details.

Table 1: Carbon and blank column details.

Column	Weight	Length	Initial NH ₃ Concentration
BAC	9.43 g	9.25 cm	7.05 mg/min
Vapure	8.14 g	8.75 cm	6.87 mg/min
Sand	15.0g*	5.0 cm	N/A

* The weight of the sand and length of the column was determined in order to match the flow rates of the carbon columns.

Ammonia emission analysis. Litter emissions and carbon efficacy were evaluated using 50 g fresh litter samples in the laboratory using a chamber acid trap (CAT) system. The CAT system provides a straightforward method for determining differences in NH₃ evolution by capturing off-gases in H₃BO₃. The particular arrangement (Figure 3) is similar to Moore et al. (1996) and was previously used to compare litter and cake NH₃ losses (Miles et al., 2006). Twelve air-tight chambers, 1000 ml each, receive humidified air from a single manifold. Weighed litter samples were placed in each air tight chamber. To assess litter NH₃ generation, exhaust air from each chamber flowed through a series of two H₃BO₃ flasks at approximately 115 ml/min. The solution from the two flasks was combined into a single sample and titrated with HCl as above. The NH₃ trapped in solution was reported as mg N recovered. For estimating carbon column efficiency, the columns described above were loaded with BAC and Vapure carbons and placed in the exhaust flow between the chambers and acid traps. The column details and average exhaust flows are reported in Table 2. The treatments as no column (litter only-control), BAC and Vapure columns were randomly assigned to the chambers in the CAT system and each replicated three times. All treatments were titrated each morning and afternoon at consistent times for the three day test period.

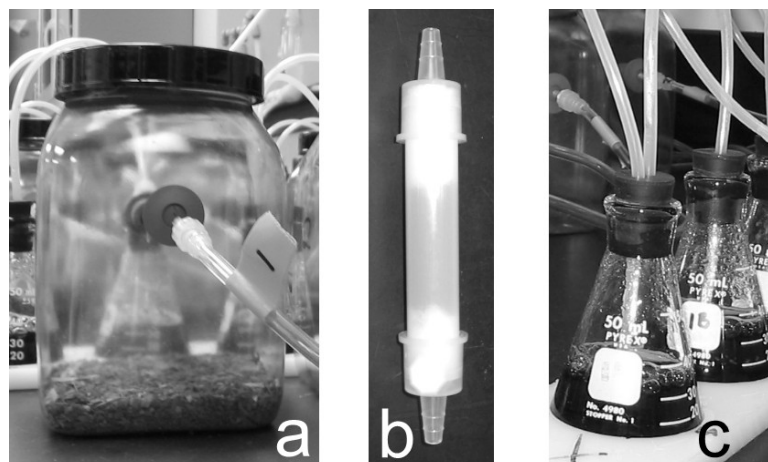


Figure 3. Chamber acid-trap system for capturing NH_3 in the laboratory: a) litter in chamber, b) activated carbon column, and c) boric acid traps.

Table 2: Column details and average exhaust flow for the litter ammonia emission analysis.

Column	Weight (g)	Length (cm)	Litter Weight (g)	Humidified Air Flow (mL/min)
BAC				
1	5.05	4.90	50.02	113.0
2	4.98	5.00	50.01	114.0
3	5.04	4.80	50.00	90.2
Vapure				
1	5.00	6.00	50.00	67.6
2	5.05	6.00	50.01	63.3
3	5.05	5.50	50.01	101.8

Results and Discussion

In the direct NH_3 adsorption phase tests, it was discovered the carbon from broiler litter performed better than the commercial carbon with regard to NH_3 adsorption. The broiler litter carbon resisted breakthrough 21% longer than the Vapure 612, the commercial carbon. At the high flow rate, the Vapure carbon experienced breakthrough after 50 seconds while the broiler litter carbon did not reach breakthrough until 63 seconds. The concentration of the NH_3 gas was 7.05 mg N/min for the broiler litter assessment and 6.87 mg N/min for the Vapure trial. Saturation ($C/C_o = 1.0$) was achieved by both carbons within 10 minutes. The removal rates were 0.98 mg N/min for the BAC which was the maximum allowed by the experimental flow rates for 20 minutes resulting in a total of 19.6 mg of N adsorbed. The rate of adsorption of the Vapure carbon at 0.42 mg N/min was less than half of that of the BAC. This resulted in the total adsorption of 8.3 mg of N at saturation. Overall, the preliminary direct NH_3 adsorption testing indicated the BAC performed approximately twice as good as the commercial source (Table 3).

Table 3: Direct ammonia adsorption results.

Sample ID	Total Adsorption (mg N)	mg N Adsorbed/ gram Carbon	Breakthrough Time (seconds)
BAC	19.6	2.07	63
Vapure	8.3	1.02	50

Based on the direct NH_3 adsorption phase testing, it was decided the broiler litter carbon performed well enough to test with litter emissions. The litter was collected as described above and carbon columns or litter only were set up within the CAT system. In the litter ammonia emission testing, the commercial carbon again reached breakthrough before the BAC, evidenced by the color change in the Vapure column acid traps noted within 2.5 hours of the test start. At the next observation, 14 hours after test start, breakthrough was visible for the BAC columns also. Litter emissions are reported as cumulative NH_3 (mg N) captured over time (Figure 4). Ammonia generated by the control litter samples after 14 hours was 4.6 mg N, whereas the BAC columns allowed an average of 2.0 mg N and the Vapure columns 2.5 mg N. At 62 hours, the control litter had emitted a total of 13.6 mg N with a standard deviation of ± 0.26 mg N. The BAC adsorbed a total of 3.4 mg N and the Vapure adsorbed 4.9 mg N. Thus, the NH_3 emission reductions using the activated carbon columns were 25% for BAC and 36% for Vapure. The uncertainty associated with both carbons for the litter emission measurements was ± 0.07 mg N.

In Figure 4 below, the similarities between the two carbon sources should be noted. The control generated more NH_3 than when the litter emission was captured using either activated carbon column. Though the BAC achieved breakthrough later than the Vapure, which indicates better initial performance, the Vapure carbon was able to surpass the BAC over time. However, the two did not appear statistically different until the final measurement at 62 hours ($p=0.0234$).

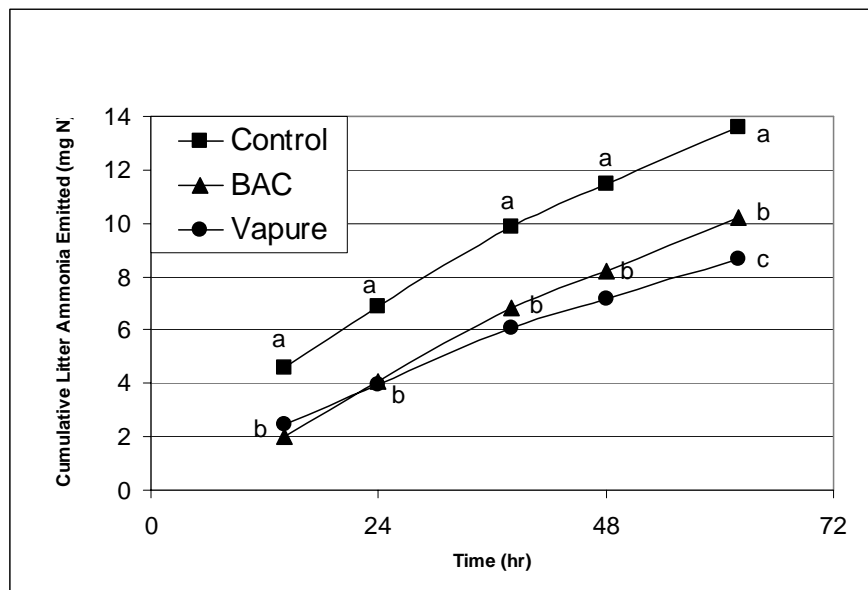


Figure 4. Cumulative litter ammonia emission for the litter only (Control), broiler activated carbon column (BAC), and commercial carbon column (Vapure). ^{a,b} Means having unlike superscripts differ significantly based on LSD comparisons ($P \leq 0.05$).

Conclusion

Activated carbon made from broiler litter is efficacious for NH_3 adsorption originating from litter. Broiler activated carbon performed better than commercial Vapure carbon in preliminary tests, but was comparable to the commercial carbon in the litter emission study. The results indicate the similarities of the carbons, though time plays a key role. This is important when examining the application of the carbon to actual broiler house emissions. In order to use this mechanism as a means for improving bird health by the reduction of ammonia in the houses, the carbon should be applied directly to the litter. However, if emissions standards are the primary concern, the carbon should be used via a filtration system at the air-flow exhausts of the houses. The cost-value comparison between the BAC and the commercial source is also a factor to be taken into consideration. The BAC represents the re-use of a waste material, deriving inherent value not only from its role as a carbon, but also as a disposal mechanism for the poultry waste itself.

Though further investigations are needed and economics of scale-up must be derived, the research demonstrates the potential for litter reuse to treat the problem of NH_3 emission to the environment and within broiler facilities.

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